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A new detector for mass spectrometry: Direct detection of low energy ions using a multi-pixel photon counter

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A new type of ion detector for mass spectrometry and general detection of low energy ions is presented. The detector consists of a scintillator optically coupled to a single-photon avalanche photodiode (SPAD) array. A prototype sensor has been constructed from a LYSO ($Lu_{1.8}Y_{0.2}SiO_5(Ce)$) scintillator crystal coupled to a commercial SPAD array detector. As proof of concept, the detector is used to record the time-of-flight mass spectra of butanone and carbon disulphide, and the dependence of detection sensitivity on the ion kinetic energy is characterised. © *2012 American Institute of Physics*. [doi:10.1063/1.3676164]

Detectors for low energy (0–10 keV) ions are required in many areas of gas-phase physics, chemistry, and analytical sciences, with mass spectrometry forming a key application area. Most detectors rely either on direct detection of ion charge or current or on detection of a cascade of electrons initiated by an ion impact. In the former category, Faraday plate or cup detectors are simple, low-cost, and robust, but suffer from relatively low sensitivity, with even state-of-the-art detectors of this type requiring around 6000 ions s^{-1} in order to record a detectable signal.[1] Recent developments include the work of Lorincik *et al.*,[2] in which a micro-array of Faraday plates coupled to a CMOS readout chip was used to record secondary ion mass spectra of a silicon sample with a detection limit of 230 counts s^{-1}. In the latter category, most modern research-grade mass spectrometers employ either an electron multiplier or a microchannel plate (MCP) detector. In both of these detectors, an ion impact elicits an electron cascade, leading to amplification of the detected current by many orders of magnitude. Such detectors are highly sensitive, with single-ion detection capabilities, and when coupled with suitable readout electronics, MCPs are also capable of position-sensitive detection with spatial resolution of tens of microns. However, they are both expensive and rather fragile, requiring a clean vacuum of better than 10^{-5} Torr for reliable operation. In addition, MCPs have a maximum output current,[3] which limits the maximum ion count rate to around 10^8–10^9 counts cm^{-2} s^{-1}. This sets an upper bound on data acquisition rates that mass spectrometer manufacturers and end users alike would very much like to overcome.

The ideal ion detector for mass spectrometry would exhibit the positive attributes of both Faraday and electron-multiplying detectors, namely, ruggedness, low cost, and high sensitivity. Recent developments in silicon technology provide a possible route to such a detector. Here we present proof-of-concept results in which a commercial single-photon-counting silicon detector coupled to a scintillator was used to record time-of-flight mass spectra of carbon disulphide and butanone. Operation of the detector is based on an ion incident on the scintillator causing emission of light, which is then detected by the silicon sensor. Scintillators are more commonly used for the detection of high energy particles in the MeV energy range or higher, rather than in the 0–20 kV range relevant to mass spectrometry. Ions in the keV energy range are stopped within the first few nanometres of the scintillator surface, and generate only a few photons, or at best a few tens of photons, per keV, depending on the scintillator type. Quenching effects for ions also reduce the scintillator detection efficiency relative to that for minimum ionizing particles such as electrons.[4] Taken together, these effects mean that scintillators are relatively inefficient for the detection of low energy ions. However, by exploiting the single-photon counting ability of state-of-the-art silicon sensors in detecting the scintillator emission, we show that high efficiency ion detection may be achieved. The resulting sensor provides an alternative to scintillator-photomultiplier and phosphor-photomultiplier detectors, which are commonly used for the detection of high energy ions, and have also been investigated for the detection of lower energy ions in applications such as recoil spectroscopy[5] and plasma diagnostics.[6]

The detector arrangement is shown in Figure 1. The silicon detector employed for the measurements was a Hamamatsu multi-pixel photon counting (MPPC) sensor (Hamamatsu MPPC S10362-11-025C). The sensor comprises an array of single-pixel avalanche photodiodes (SPADs) connected together in parallel such that the total output from all of the pixels forms the MPPC output. The sensor has an active area of 1 mm^2, with a pixel pitch of 25 μm, and is encapsulated in a layer of silicone rubber to protect the bond wires. For the measurements described here, a 1.5 $\times$ 1.5 $\times$ 0.2 mm^3 LYSO ($Lu_{1.8}Y_{0.2}SiO_5(Ce)$) scintillator

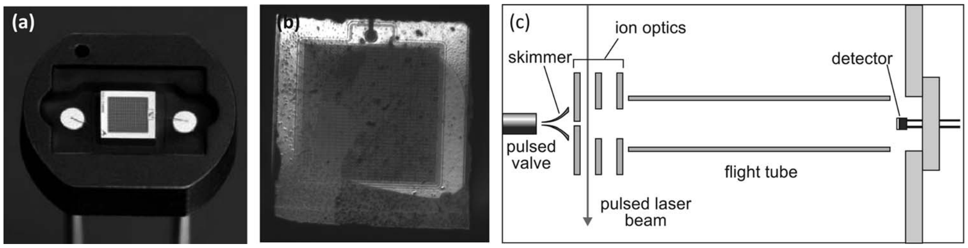

FIG. 1. (a) MPPC sensor as purchased from Hamamatsu (photo taken from Hamamatsu sales brochure); (b) close up view of MPPC optically coupled to a LYSO scintillator; (c) Schematic of the time-of-flight mass spectrometer.

crystal was attached to the front face of the MPPC using a small amount of optical grease. The emission spectrum of the scintillator extends from 390 nm to beyond 470 nm, peaking at around 420 nm.[7] The sensor was mounted on the vacuum side of a DN40 ($2\frac{3}{4}''$) ConFlat flange and connected to its readout board on the reverse of the flange via a six-pin electrical feedthrough. Data acquisition was through the manufacturer-provided USB interface software, which allows for viewing and acquisition of either the analogue or digitised (photon counted) signal from the sensor.

The detector was mounted on a home-built time-of-flight imaging mass spectrometer, which has been described in detail previously.[8] When used in combination with a position-sensitive MCP-based detector, the spectrometer is capable of recording mass-selected images of the velocity or spatial distributions of ions at their point of formation. However, for these experiments the instrument was operating in simple time-of-flight mode in order to test the new detector. The analyte of interest was seeded (with a seeding ratio of 2.5% for CS_2 and 5% for butanone) in a molecular beam of argon at a stagnation pressure of 1 bar, yielding internally cold molecules with little rotational or vibrational excitation. The molecular beam was intersected within the time-of-flight ion optics assembly by a 193 nm laser beam from a Neweks PSX100 excimer laser (1.5 mJ per 5 ns pulse). Fragmentation and ionization occurred within the intersection region, and the resulting ions were extracted along a flight tube to the detector. The extraction potential was variable from 0-10 kV. Signal was typically acquired and averaged over 256 laser shots at a repetition rate of 20 Hz.

The detector is highly sensitive to scattered photons from the 193 nm laser pulse used in the ionization step, which manifests as a large signal at very short times. While we do not have a complete explanation for the rather strange morphology of the laser-induced signal, it appears to arise solely from an interaction between scattered photons from the laser pulse and the detector. The signal disappears when the laser pulse is blocked from entering the mass spectrometer or when the scintillator is removed, and the appearance time of the signal is independent of the ion extraction potential, indicating that it does not arise from ions formed from background gas within the vacuum system. Rather than speculate further on the origins of the complex response of the detector to the laser pulse, the laser-induced signal will be investigated systematically in future experiments. In any case, by recording time-of-flight traces with the molecular beam on and off, this artefact may be removed extremely reliably to leave the time-of-flight mass spectrum of the analyte of interest. A complete data set of this type recorded for the butanone molecule at an extraction potential of 8 kV, together with the difference signal and a spectrum recorded using a conventional microchannel plate detector, is shown in Figure 2. The signal arising purely from the ionization laser pulse, which is removed by the background subtraction, can be identified as the initial sharp peak at $t \approx 150$ ns, corresponding to the time when the laser fires, together with a large amorphous (saturated) signal which appears a few hundred nanoseconds later. The

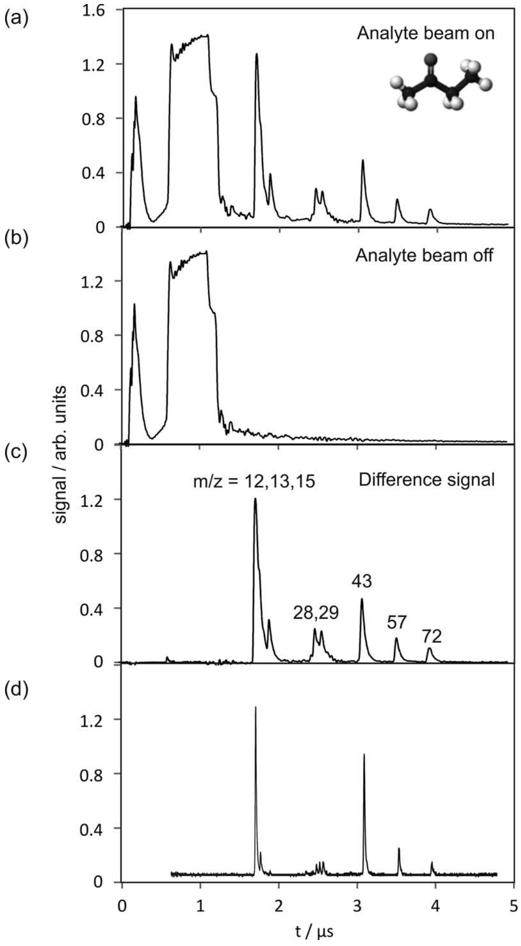

FIG. 2. Time-of-flight spectrum of butanone recorded using the sensor: (a) molecular beam on; (b) molecular beam off; (c) difference signal; (d) spectrum recorded using a conventional microchannel plate detector, for comparison. Note that the ionization pulse (which gives rise to a large "background" signal) occurs at $t \approx 150$ ns, and ion flight times should be calculated relative to this time.

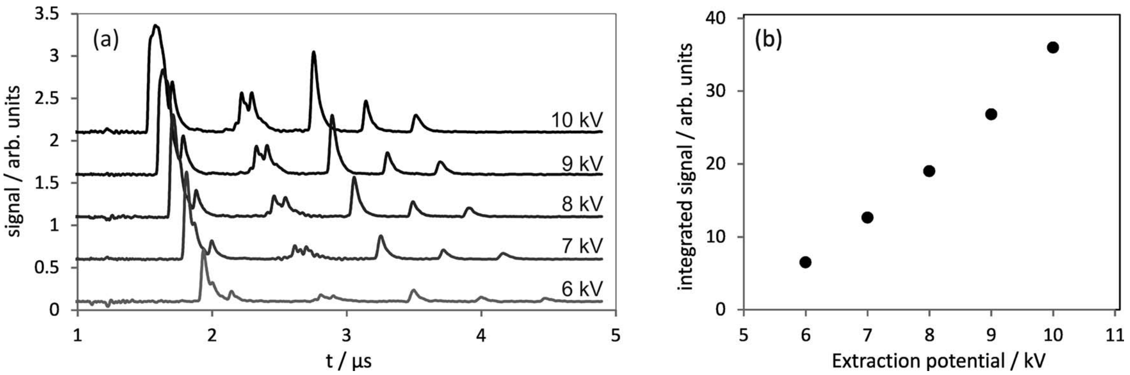

FIG. 3. (a) Mass spectra recorded for butanone as a function of ion extraction potential (successive spectra have been offset for clarity); (b) total integrated signal as a function of extraction potential (see text for details). The ion lens potentials are such that the true ion energies are only very slightly less than the extraction potentials quoted in the figure.

data were recorded via the analogue output of the MPPC sensor. The intrinsic time resolution of the MPPC is extremely high, stated by the manufacturer as 200-300 ps, making these sensors ideal for applications in mass spectrometry. However, in our hybrid scintillator/MPPC sensor the achievable mass resolution is limited by the ∼40 ns decay lifetime of the scintillator, with the exponential decay of the scintillator clearly visible as a "tail" in the time-of-flight peaks. Nevertheless, all of the various fragment peaks are clearly resolved in the mass spectrum. In the future we plan to test other scintillators with shorter decay lifetimes (for example, BaF_2 has scintillation times as short as 0.7 ns), which will lead to an improvement in the time-of-flight – and therefore mass – resolution achievable with sensors of this type. We also envisage developing an integrated version of the sensor, in which the scintillator is deposited directly onto the surface of the SPAD array in order to improve the optical detection efficiency.

The response of the scintillator, and consequently the detector as a whole, has a strong, almost linear dependence on the kinetic energy of the incident ions, as determined by the ion extraction potential. We have characterised this energy dependence by recording the butanone mass spectrum at a range of energies from 6 kV to 10 kV. The results are shown in Figure 3. The mass spectra recorded at each extraction potential are shown in Figure 3(a), while Figure 3(b) shows the total integrated signal intensity over all but the first mass peak. The first peak was excluded from the analysis as the number of photons emitted from the scintillator saturates the MPPC sensor electronics (Hamamatsu module C10507-11-025C) at the highest extraction potentials. The electronics are known to saturate at signal levels greater than 10 p.e. (p.e. = "photon equivalents"), indicating that for the remaining (unsaturated) mass peaks we detect less than 10 p.e. per time-of-flight cycle. The total signal increases by around a factor of seven as the extraction potential is increased from 6 to 10 kV, and shows the expected almost linear dependence on ion kinetic energy. Though ion signals could be detected down to extraction potentials as low as 4 kV, the signal-to-noise ratio was very poor at these low energies. While there is no straightforward way for us to determine the absolute detection efficiency of our hybrid sensor using the mass spectrometer in its current configuration, the single photon counting capabilities of SPAD-based sensors mean that so long as the ion kinetic energy is sufficiently high to excite the scintillator, the light collection efficiency is reasonably high, and the electronics threshold sufficiently low, detection efficiencies of close to 100% should be achievable.

Finally, to demonstrate that it is indeed the hybrid scintillator/MPPC sensor generating the ion signals, and that the MPPC itself is not sensitive to ion impact (though we note that in the initial configuration the energy of the ions should be insufficient to penetrate the scintillator and reach the MPPC), the scintillator was removed from the front face of the MPPC sensor, and signals detected in the presence and absence of the scintillator were compared. Figure 4 shows mass spectra recorded for CS_2 using the scintillator/MPPC sensor and the bare MPPC sensor. On removing the scintillator, the ion signal all but disappears. The trace taken in the absence of scintillator was recorded under conditions that maximised the signal intensity, and should be divided by a factor of five to ten in order to carry out a direct comparison between the two data

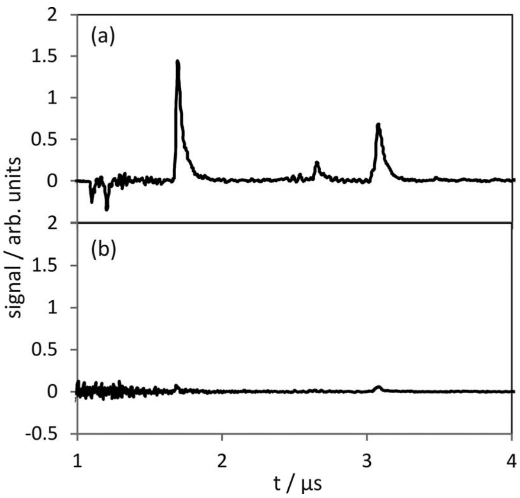

FIG. 4. Time-of-flight signals recorded using the MPPC sensor for CS_2 in (a) the presence and (b) the absence of the scintillator crystal. The lower trace was recorded under conditions, which maximised the signal intensity, and should be divided by a factor of five to ten in order to carry out a direct comparison with the upper trace. The negative peaks near the start of the upper trace are an artefact of the background subtraction procedure.

sets. We believe that any residual signal is most likely due to low-level scintillation either from optical grease residue on the front face of the MPPC, or from the silicone rubber encasing the sensor.

While currently still in their infancy, once developed into a mature technology, silicon-based ion detectors of the type demonstrated here in proof-of-concept are likely to have a number of potential advantages over microchannel plate detectors. Perhaps the most important is their robustness, in particular, their ability to operate at pressures up to atmospheric pressure and higher. This opens up intriguing possibilities for new mass spectrometric techniques operating in a higher pressure regime than traditional methods. Silicon sensors will also be considerably lower in cost than traditional ion detectors, since their production may be automated in the same way as any other silicon technology. Large-area detectors will improve detection efficiency for ion beams larger than the 1 mm^2 detector employed here. SPAD-based imaging sensors, consisting of two-dimensional arrays of independent SPAD pixels, are currently under development, and SPAD arrays coated with a thin layer of scintillator will provide a competitive alternative to conventional MCP-phosphor or MCP-delay-line detectors for ion imaging measurements.

In summary, we have demonstrated a new type of ion detector for mass spectrometry, based on a scintillator optically coupled to a single-photon avalanche photodiode array. As proof-of-concept, the detector has been used to record time-of-flight mass spectra of small organic molecules, and has been shown to perform well for ion energies above around 5 keV.

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[1] P. Amico, J. W. Beletic, and J. E. Beletic, *Scientific Detectors for Astronomy: The Beginning of a New Era* (Springer, New York, 2004), p. 332.
[2] J. Lorincik, M. B. Denton, R. P. Sperline, E. T. Young, and P. Williams, Anal. Lett. **44**(6), 1050 (2011).
[3] W. B. Feller, Nucl. Instrum. Methods Phys. Res. A **310**, 249 (1991).
[4] H. O. Funsten, S. M. Ritzau, R. W. Harper, and R. Korde, App. Phys. Lett. **84**(18), 3552 (2004).
[5] M. N. Akhtar, B. Ahmad, and S. Ahmad, Nucl. Instrum. Methods Phys. Res. B **207**, 333 (2003).
[6] D. Jiménez-Rey, B. Zurro, L. Rodríguez-Barquero, A. Baciero, and M. Navarro, Rev. Sci. Instrum. **81**, 10D317 (2010).
[7] I. G. Valais, C. M. Michail, S. L. David, A. Konstantinidis, D. A. Cavouas, I. S. Kandarakis, and G. S. Panayiotakis, IEEE Trans. Nucl. Sci. **55**(2), 785 (2008).
[8] W. S. Hopkins, M. L. Lipciuc, S. H. Gardiner, and C. Vallance, J. Chem. Phys. **135**, 034308 (2011).